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SHORT COMMUNICATIONS

Solubilization of Hibitane into Common Organic Solvents with Self-Assembled Fluorinated Molecular Aggregates. Application to Novel Surface Antibacterial Materials Possessing a Good Oleophobicity

Hideo SAWADA,[*,**,†,††] Kenta YANAGIDA,[**] Ryo TAKAHASHI,[***]
Yoshikazu NISHIKAWA,[***] Tokuzo KAWASE,[***] Kazuya OHARU,[****]
Hideki NAKAGAWA,[****] Kunihiro OHIRA,[****] and Kunimi WADA[*****]

[*]*Department of Chemistry, Nara National College of Technology, Yata, Yamatokoriyama, Nara 639–1080, Japan*
[**]*Department of Chemistry, Faculty of Advanced Engineering, Nara National College of Technology, Yamatokoriyama, Nara 639–1080, Japan*
[***]*Graduate School of Human Life Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558–8585, Japan*
[****]*Asahi Glass Co., Ltd., Yurakucyo, Chiyoda-ku, Tokyo 100–8405, Japan*
[*****]*Japan Synthetic Textile Inspection Institute Foundation, Edobori, Nishi-ku, Osaka 550–0002, Japan*

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The development of new polymeric functional materials possessing surface antibacterial activities has hitherto been desired from the practical point of view.[1] Fluorinated polymeric compounds containing cationic segments are expected to apply to novel fluorinated polycationic biocides possessing both the surface antibacterial activity and the surface active property imparted by fluorine. In fact, we have very recently reported that fluoroalkyl end-capped cooligomers containing dimethyl(octyl)ammonium segments are applicable to new fluorinated functional materials possessing not only the surface antibacterial activity but also the surface active property imparted by fluorine.[2] Thus, it is very interesting to explore novel fluorinated polymeric biocides possessing surface active property imparted by fluorine. Previously, we reported that fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (DOBAA) oligomers can form the molecular aggregates imparted by the aggregation of end-capped fluoroalkyl segments in organic media, and this fluorinated self-assembled molecular aggregates can recognize selectively hydrophilic amino and *N,N*-dimethylamino compounds as guest molecules.[3] It is well known that hibitane: 1,1′-hexamethylenebis{[5-(4-chlorophenyl)biguanide]dihydrochloride} is a derivative of guanidine and this compound is a potent low-molecular weight biocide.[4] However, this potent biocide exhibits an extremely poor solubility in common organic solvents except for methanol. Therefore, it is in general difficult to apply this biocide to the common polymeric antibacterial materials. In the course of our comprehensive studies on the development of novel fluorinated polymeric antibacterial materials, we have found that the self-assembled molecular aggregates formed by fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers [R_F–(DOBAA)$_n$–R_F] can solubilize hibitane into common organic solvents, and the modified polystyrene surface with the fluorinated aggregates-hibitane complex exhibited a good surface antibacterial activity. These results will be described herein.

Following is a typical experimental procedure for the solubilization of hibitane into common organic solvents by the use of R_F–(DOBAA)$_n$–R_F, which were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding DOBAA monomer according to our previously reported method.[3] To an 1,2-dichloroethane solution of R_F–(DOBAA)$_n$–R_F [R_F = $CF(CF_3)OC_3F_7$: M_n = 6900 (2 g dm^{-3}: 5 mL)] was added hibitane

[†]To whom correspondence should be addressed.
[††]Present Address: Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, 3 Bunkyocyo, Hirosaki 036–8561, Japan.

(5 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. The organic solution thus obtained was centrifuged for 30 min, and then the residual hibitane was filtered through a 0.45 μm PTFE filter membrane to obtain a colorless organic solution. UV-Vis spectra of organic solution of hibitane solubilized with R_F–$(DOBAA)_n$–R_F showed an absorption band around 280 nm, although hibitane in methanol was detected by UV absorption around 260 nm and R_F–$(DOBAA)_n$–R_F showed no absorption band from 250 to 340 nm, as in Figure 1.

The amounts of solubilized hibitanes were estimated by the use of UV-Vis spectra, and the solubilized hibitanes with R_F–$(DOBAA)_n$–R_F were as follows:

R_F in oligomer $CF(CF_3)OC_3F_7$	the added hibitane (mg)	solubilization ratio of hibitane (%)[a)]
	1	33
	2	13
	5	10
	10	3.5
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (M_n = 7900)		
	1	6.1
	2	3.7
	10	1.0
	20	0.5

a) based on the added hibitane

In contrast, the corresponding non-fluorinated DOBAA polymer [–$(DOBAA)_n$–: M_n = 29000] showed no solubility of hibitane into 1,2-dichloroethane under similar conditions.

The red-shift of UV-vis spectra from 260 nm to 280 nm in Figure 1 suggests that the self-assembled molecular aggregates of R_F–$(DOBAA)_n$–R_F in 1,2-dichloroethane can interact strongly with hibitane as a guest molecule. In fact, the dynamic light scattering measurements showed that the size (mean diameter) of molecular assemblies formed by R_F–$(DOBAA)_n$–R_F in 1,2-dichloroethane solutions is from 300 to 600 nm, and especially, the size of the fluorinated aggregates [R_F = $CF(CF_3)OC_3F_7$] is from 380 nm to 444 nm as shown in Figure 2. The decrease of the size of the molecular assemblies formed by the solubilization of hibitane in each concentration of oligomer (see Figure 2) indicates that the self-assemblies of R_F–$(DOBAA)_n$–R_F could interact with hibitane as a guest molecule to form the host-guest intermolecular complex. On the other hand, we cannot observe the forma-

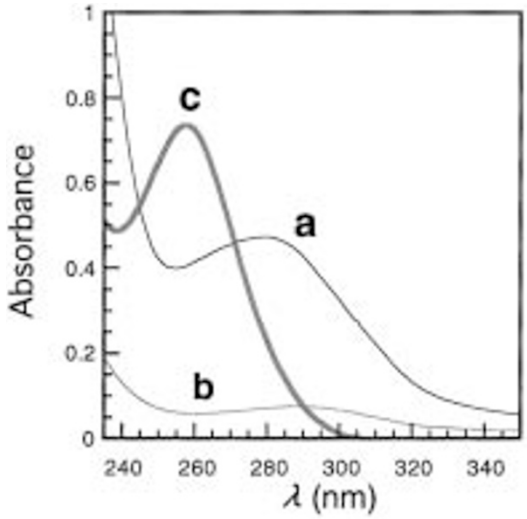
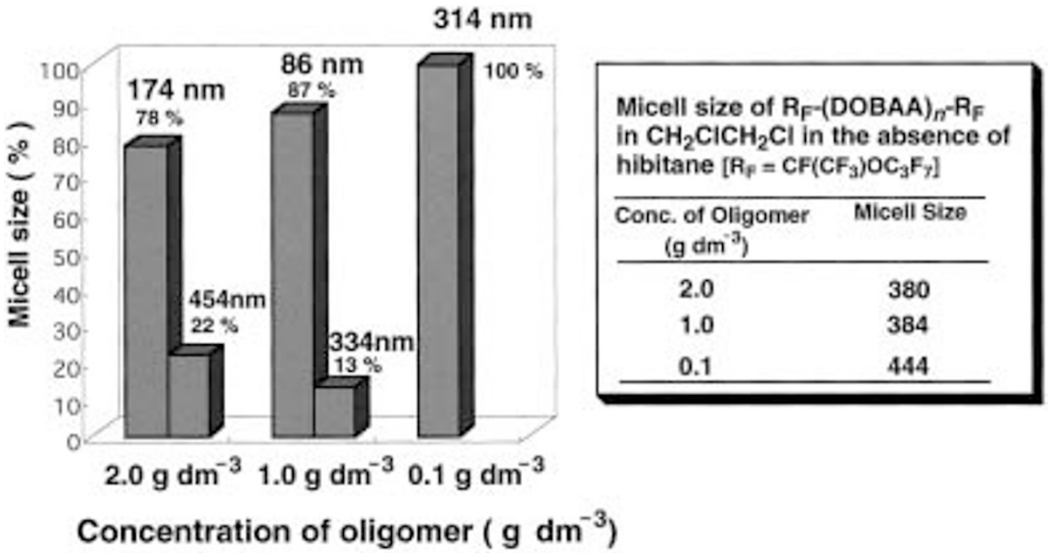


Figure 1. UV-vis spectra of solubilized hibitane into 1,2-dichloroethane by fluoroalkyl end-capped DOBAA oligomer. a: Solubilized hibitane into 1,2-dichloroethane by R_F–$(DOBAA)_n$–R_F oligomer (2 g dm^{-3}: R_F = $CF(CF_3)OC_3F_7$). b: CH_2ClCH_2Cl solution of R_F–$(DOBAA)_n$–R_F oligomer (2 g dm^{-3}: R_F = $CF(CF_3)OC_3F_7$). c: MeOH solution of Hibitane (400 mg dm^{-3}).



Micell size of R_F-$(DOBAA)_n$-R_F in CH_2ClCH_2Cl in the absence of hibitane [R_F = $CF(CF_3)OC_3F_7$]

Conc. of Oligomer (g dm^{-3})	Micell Size
2.0	380
1.0	384
0.1	444

Figure 2. Micell size distributions of R_F–$(DOBAA)_n$–R_F[R_F=$CF(CF_3)OC_3F_7$] CH_2ClCH_2Cl solutions including hibitane.

Table I. Contact angle of dodecane on PSt films treated with self-assembled molecular aggregates of R_F–$(DOBAA)_x$–R_F[R_F = $CF(CF_3)OC_3F_7$][a] including hibitane[a,b]

Solubilized hibitane	Contact Angle (Degree)
0.35 mg	10
0.33 mg	15
–$(DOBAA)_n$–	0
PSt	0

[a]The PSt films were prepared by casting 1,2-dichloroethane solutions of PSt and oligomer containing hibitane on a glass plate. The solvent was evaporated at room temperature, and the file formed peeled off and dried at 50 °C for 24 h under vacuum. [b]Concentration of oligomer based on PSt is 1% (m/m).

tion of the micell of the corresponding non-fluorinated DOBAA polymer[–$(DOBAA)_n$–] under similar conditions.

Therefore, our present fluorinated aggregates-hibitane complexes are expected to develop into new fluorinated surface active compounds for common polymeric materials such as polystyrene (PSt). In fact, the fluorinated aggregates-hibitane complexes were tested for the surface activity as a new type of surface modification agents, and the results are as following.

As shown in Table I, contact angle of dodecane on the cast film of Pst treated with the fluorinated aggregates-hibitane complexes showed a significantly large value (10–15°) compared with that non-treated Pst (0°) or that non-fluorinated DOBAA polymer (0°). This finding suggests that these fluorinated complexes exhibit a markedly strong oleophobicity on the surface, and we can develop these complexes into new fluorinated surface modification agents possessing antibacterial activity. Especially, hibitane in these fluorinated complexes could be also arranged above the surface.

Thus, we investigated the surface antibacterial activity of Pst film treated with these fluorinated complexes against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). In general, the compounds, which are capable of killing the bacterial cells from 10^9 to 10^6 cfu (colony forming units), are considered to possess an antibacterial activity. Our present Pst films treated with fluorinated aggregates [R_F–$(DOBAA)_n$–R_F; R_F = $CF(CF_3)OC_3F_7$ (2 g dm^{-3}: 5 mL)]-hibitane (solubilized hibitane: 0.35 mg) complexes [concentration of oligomer based on Pst is 1% (m/m)] were capable of killing the bacterial cells from 1.4×10^9 cfu to 1.6×10^4 cfu (*E. coli*), and 8.0×10^8 (cfu) to 3.6×10^5 cfu (*S. aureus*), respectively.

In this way, our present self-assemblies formed by R_F–$(DOBAA)_n$–R_F oligomers were demonstrated to interact with hibitane, which exhibits an extremely poor solubility in common organic solvents except for methanol, to form the host-guest complexes. These fluorinated aggregates-hibitane complexes are easily soluble in common organic solvents such as 1,2-dichloroethane and chloroform. In particular interest, these fluorinated complexes are applicable to a new type of surface modification agents for well-known polymeric materials such as Pst, and the Pst surface treated with these complexes were formed to possess a good antibacterial activity with a good oleophobicity imparted by fluorine. Further studies are actively in progress.

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